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A Shortened Type "C" Process (Characteristics of a Combined Bleach-Fix)

Donald Sykes

A SHORTENED TYPE "C" PROCESS

(Characteristics of a Combined Bleach-Fix)

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Senior Research

Rochester Institute of Technology

666 Amherst Street
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May 19, 1958

Messrs. Shoemaker, Todd
Rochester Institute of Technology
65 Plymouth Avenue
Rochester, New York

Dear Messrs. Shoemaker and Todd,

The enclosed report is being submitted as a part of the fourth year Photo Science Senior Research Course, at the Rochester Institute of Technology.

The author feels that this report adequately surveys the scope of the investigations and results acquired during the limited period of time available.

Respectfully

Donald J. Sykes

Abstract

The theory of combined bleach-fix bathes is discussed with an explanation of the function of sequestrene. Three investigations are described were the components of the solutions are varied, and the results stated. Formulas of successful bleach-fix baths used with a Kodak P122 Process are given.

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Illustrations and Graphs

Introduction

The conception and development of modern color photographic process have provided the photographic industry with a dynamic new tool. Along with its many advantages, color photographic processes have presented a host of new problems.

One of the many problems or disadvantages these color processes have brought is that of extended processing time. It was the author's intention to find an area or areas that might practically be combined or shortened. One of the popular tripack color materials on the United States market today, Kodak's P122 color print process, was chosen for the investigation.

Through an intensive literature search, it was learned that some work had been done in the European photographic industry, with attempts to shorten color processingtime. [1]The methods described for shortening these processes revolved around either the use of a more energetic color developing solution or the use of a combined bleach-fix bath. The latter was chosen as the area of investigation for this paper.

Theory

The combination of a bleaching and fixing agent immediately presents a basic chemical problem. The bleaching agent being an oxidizing agent and the fixing agent being a reducing agent, the two will react with each other and cause an early exhaustion of the bath. This is shown in equation 1.

$$(1) \quad (2Fe^{+3} + 2S_2O_3^{-2} \longrightarrow 2Fe^{+2} + S_4O_6^{-2})$$

As a result of the investigations of[2] Gerald Schwarzenbach and Arthur Martell, a method was found that could be applied to the above stated problem; i.e. an oxidizing and reducing agent could be compounded in the same solution with the aid of a chelating agent. The chelating agent acts as a protecting element, in this case, around the oxidizing agent, Fe^{+3}, thus protecting the oxidizing agent from reaction with silver halides solvent, and thereby, exhausting the combined bath. The complexing agent investigated by Schwarzenbach and Martell was ethylene diamine tetra-acetic acid. The structure of this is illustrated in Figure 1.

In the author's investigation, the ferric complex of ethylene diamine tetra-acetic acid was employed.

The ethylene diamine tetra-acetic acid complexing agent are available under the following trade names:

(1) Sequestrene

(2) Versene

(3) Nullapon

(4) Trilon

The author employed the Sequestrene complex manufactured by the Geigy Chemical Company.

Procedure

Early in this investigation, the already published [3]European formulas on combined bleach-fix bath were compounded and tested with the Kodak P122 materials. The information obtained here was employed as a guide in designing the first factorial investigation. (Shown in Figure 2.)

Upon the completion of this first investigation, three analysis of variances were run on the observed data, checking red, green, and blue, average gradient variances. The residuals of the investigation, in all cases, were too large. Therefore, the results of the first investigation were not significant. The author attributed this lack of any significance to the original experimental methods, i.e. as an economic measure all the runs were processed in the same developer instead of using fresh developer for each run and discarding it after use. It was also found that hand agitation in trays did not prove to be as adequate a method of testing bleach-fix variance.

As a result of this costly experience, the second investigation was designed and executed more critically. (see Figure 3)

The negative selected as a standard for the investigation served a two-fold purpose.

First, it provided a sensitometric means of evaluating the process and second, it included a visual means of process evaluation. Figure 4 is a print from the standard negative. This negative was contact printed on Type C material just prior to processing.

Exposure of material was made from the lamphouse of a Beseler 45MC enlarger onto a contact printing frame. The exposure duration was seven seconds at f5.6, with enlarger at maximum magnification using a four inch Ektar lens. Filtration consisted of an 80 yellow, 50 magenta and 2B Color Compensating filters. The exposed Type C material was processed in 250cc. each of the following solutions:

Baths	Time	Temperature
Developer - Kodak P122	12 min.	75°F.
Stop Bath - Kodak P122	2 "	75°F.
Wash	1 "	80°F.
Bleach-Fix	4 "	75°F.
Wash	5 "	80°F.

Agitation for all solutions was once every 30 seconds for 5 second duration. Temperature control was maintained at plus or minus ½ degree F. by a water bath system employing a Powers Foto-Guard temperature control unit. Tray processing was still employed for investigation number two. Throughout Investigations One and Two, the sulfite and thiourea concentrations were not varied.

A third Investigation was designed in which only iron sequestrene (E.D.T.A.) and sodium thiosulphate were included in solution; excluding the sulfite and thiourea.

Since the authorfound that tray processing was inadequate, he designed and built three plastic tanks which will accept: 1 - 500cc. of developer; 2- 500cc. of stop bath, and 3 - 250cc each of different formula bleach-fix bath in its two compartments. These tanks were constructed of one/eighth inch plexi-glass, cemented with Ducco plastic cement. (See Figure 5.)

Results

Investigation One showed no significant differences at the levels tested. As stated earlier, the author attributes this to unnecessary experimental variations i.e. the use of the same developer for all runs, and hand agitation for all process.

Investigation Two was designed to be similar to Investigation One, but it was executed more critically, i.e. fresh processing solutions were used in each run. Figure 6 lists the significant and non-significant factors resulting from nine analysisof variances incorporating the data from Investigation Two.

Analysis of the results from Investigation Two shows the following:

Effect on Average Gradient

1. Red gradient increases with increase of ferric sequestrene concentration, except at low hypo concentrations and alkaline ph.

1a. Red gradient decreases with increase of ferric sequestrene at low hypo concentrations and alkaline ph.

2. Red gradient increases with decreased hypo concentration at high ph and high iron concentration.

3. Green gradient increases with increase of ferric sequestrene concentration at high hypo concentrations.

3a. Green gradient decreases with increase in ferric sequestrene concentrations at low hypo concanctrations.

4. Green gradient increases as ph increases.

5. Blue gradient increases with increase in ferric sequestrene concentrations at high hypo concentrations.

5a. Blue gradient decreases with increase in ferric sequestrene concentration at low hypo concentration.

Effect on Maximum Density

1. The red maximum density increases with increase in ferric sequestrene concentration, except at low hypo and high ph.

1a. Red maximum densitydecreases with increase of ferric sequestrene concentration at low hypo and high ph.

2. Red maximum density increases with decrease in hypo concentration, except with high iron concentration and alkaline ph.

2a. Red maximum density increases with increase in hypo concentration at high iron concentration and alkaline p h.

3. Green maximum density not affected significantly.

4. Blue maximum density increases with increase of ferric sequestrene concentration except at low hypo concentrations and alkaline ph.

4a. Blue maximum density increase with decrease of ferric sequestrene concentration at low hypo concentration and alkaline ph.

5. Blue maximum density increases with decrease of hypo concentration except at high ferric sequestrene concentration and high ph.

5a. Blue maximum density increases with increase in the hypo concentration at high ferric sequestrene concentration and alkaline ph.

6. Blue maximum density increases slightly with increase of ph at low ferric sequestrene concentration.

6a. Blue maximum density increases with decrease of ph at high ferric sequestrene concentration.

Figure 7-8 include the graphs resulting from the plots of the factors that were considered to be affecting the quality of the dye images.

Figure 4 compares the regular Kodak Process Print with prints processed in two of the formulas the author found comparable.

Figure 9 consists of graphs, D. Log. E. curves, of the regular Kodak Process prints and those of formulas two and eight.

The affects of the eight different formulas of Investigation Two and the regular Kodak formula on gamma, D.

Max. and D. Min. are illustrated in Figures 10 and 11.

Investigation Three tested ferric sequestrene and hypo concentrations only. After twenty-four hours of aging, an excess of yellow dye resulted in each case. This is shown in the high yellow density level in Figure 12.

Discussion of Results

The results of the investigation confirmed the author's hope that the Kodak P122 Process could be successfully shortened by the introduction of a combined bleach-fix bath. The investigation has further provided the, heretofor unobtainable, information regarding the inherent characteristics of bleach-fix baths.

One of the most effective factors governing the final color balance was the time allowed for the solution to come to equilibrium, i.e. a variety of color combinations resulted depending on the length of time expired between the time of solution mixture and the time of processing. This effect was found to be very dependent on the sulfite concentration. The yellow dye layer was particularly sensitive to this equilibrium effect, i.e. yellow dye curves were displaced vertically from the normal, while the other layers were not significantly affected.

The following hypothesis are not yet proven but tend to give probable reasons for this added yellow dye density.

1. Salt Effect - particular concentrations of salt in the bleach-fix bath force the yellow dye molecules to aggragate in a particular manner which

changes the absorbency of the dye. A spectrophotometric check on the dye would reveal the answer to this question.

2. Developer Retention Effect - Since the yellow dye layer is the lower most layer in the color material investigated, any developer remaining on the material will most likely be retained in this layer. Upon placing this print in a bleach-fix bath the Fe^{+3}, is able to oxidize the remaining developer thus forming excess yellow dye.

The preceeding thoughts are worthy of further investigation. An investigation into:the permanence of prints processed by this method, the effects of thiourea and sulfite, and methods of solution regeneration will further provide us with pertinent information.

Acknowledgement

The author wishes to thank the Rochester Institute of Technology for providing the laboratory and equipment for the execution of these investigations. Particular appreciation is extended to Messrs. William Shoemaker and Hollis Todd for their guidance and cooperation towards making the foregoing investigations a success. Further thanks is due the author's friends and colleagues, whose suggestions proved to be very helpful.

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3. op.cit. Gordon; Hornsby; Finn.

FERRIC
ETHYLENE DIAMINE TETRA-ACETIC ACID
STRUCTURE

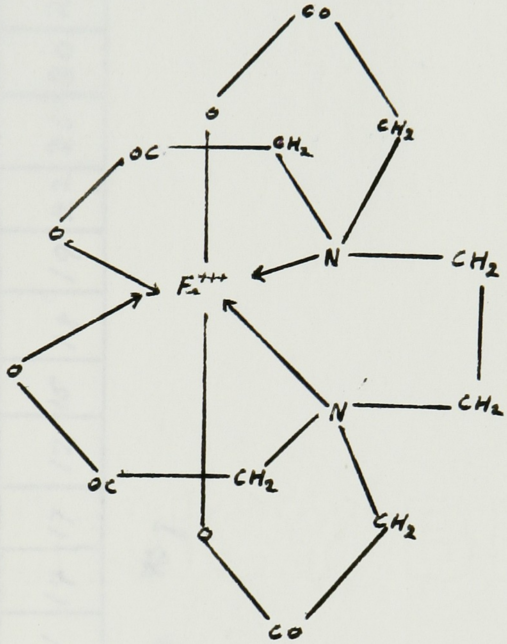


Figure 1.

	FE^{+++} 25 g/l									FE^{+++} 50 g/l									FE^{+++} 75 g/l								
	HYPO 100 g/l			HYPO 175 g/l			HYPO 250 g/l			HYPO 100 g/l			HYPO 150 g/l			HYPO 250 g/l			HYPO 100 g/l			HYPO 150 g/l			HYPO 250 g/l		
	PH 4	PH 6	PH 8	PH 4	PH 6	PH 8	PH 4	PH 6	PH 8	PH 4	PH 6	PH 8	PH 4	PH 6	PH 8	PH 4	PH 6	PH 8	PH 4	PH 6	PH 8	PH 4	PH 6	PH 8	PH 4	PH 6	PH 8
RUN	1	4	7	2	5	8	3	6	9	10	13	16	11	14	17	12	15	18	19	22	25	20	23	26	21	24	27

INVESTIGATION #1

FIGURE 2

	FE^{+++} 20 g/l				FE^{+++} 46 g/l			
	HYPO 100 g/l		HYPO 300 g/l		HYPO 100 g/l		HYPO 300 g/l	
	PH 4	PH 8	PH 4	PH 8	PH 4	PH 8	PH 4	PH 8
RUN	1	2	3	4	5	6	7	8

INVESTIGATION # 2

FIGURE 3

Formula # 2
Inv. # 2

Regular Kodak
Formula

Formula # 8
Inv. # 2

Figure 4.

PLEXIGLASS TANKS

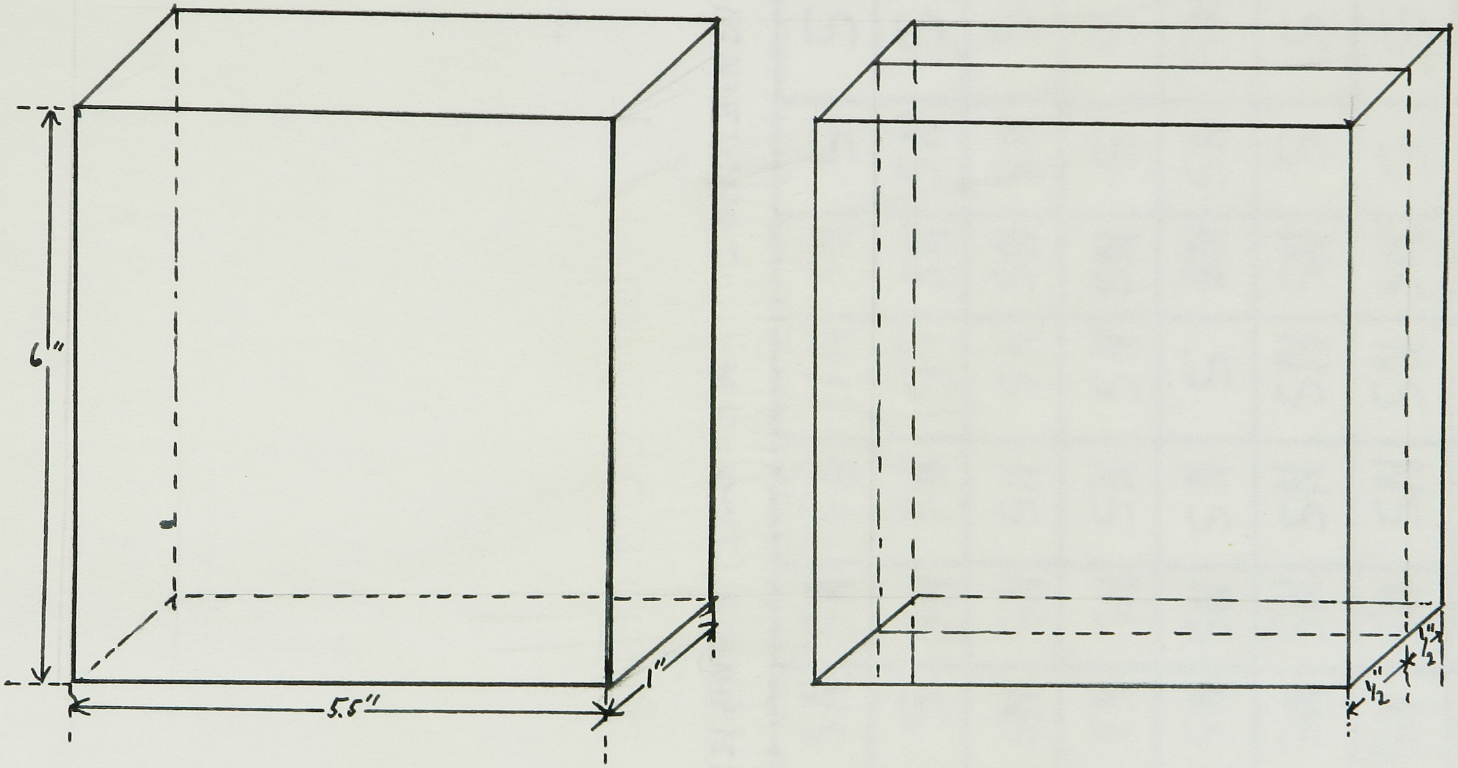


FIGURE 5

TABLE OF SIGNIFICANT FACTORS

	R			G			B		
	γ	D_{MAX}	D_{MIN}	γ	D_{MAX}	D_{MIN}	γ	D_{MAX}	D_{MIN}
Fe^{+++}	S	S	NS	NS	NS	NS	NS	S	NS
HYPO	S	S	NS	NS	NS	NS	NS	S	NS
PH	NS	NS	NS	S	NS	NS	NS	S	NS
Fe^{+++} PH	S	S	NS	NS	NS	NS	NS	S	NS
HYPO PH	S	NS	NS	NS	NS	NS	NS	NS	NS
Fe HYPO	S	NS	NS	S	NS	NS	S	S	NS
Fe · HYPO PH	S	S	NS	NS	NS	NS	NS	S	NS

S = SIGNIFICANT NS = NOT SIGNIFICANT

Figure 6.

EFFECT OF BLEACH-FIX ONGRADIENT

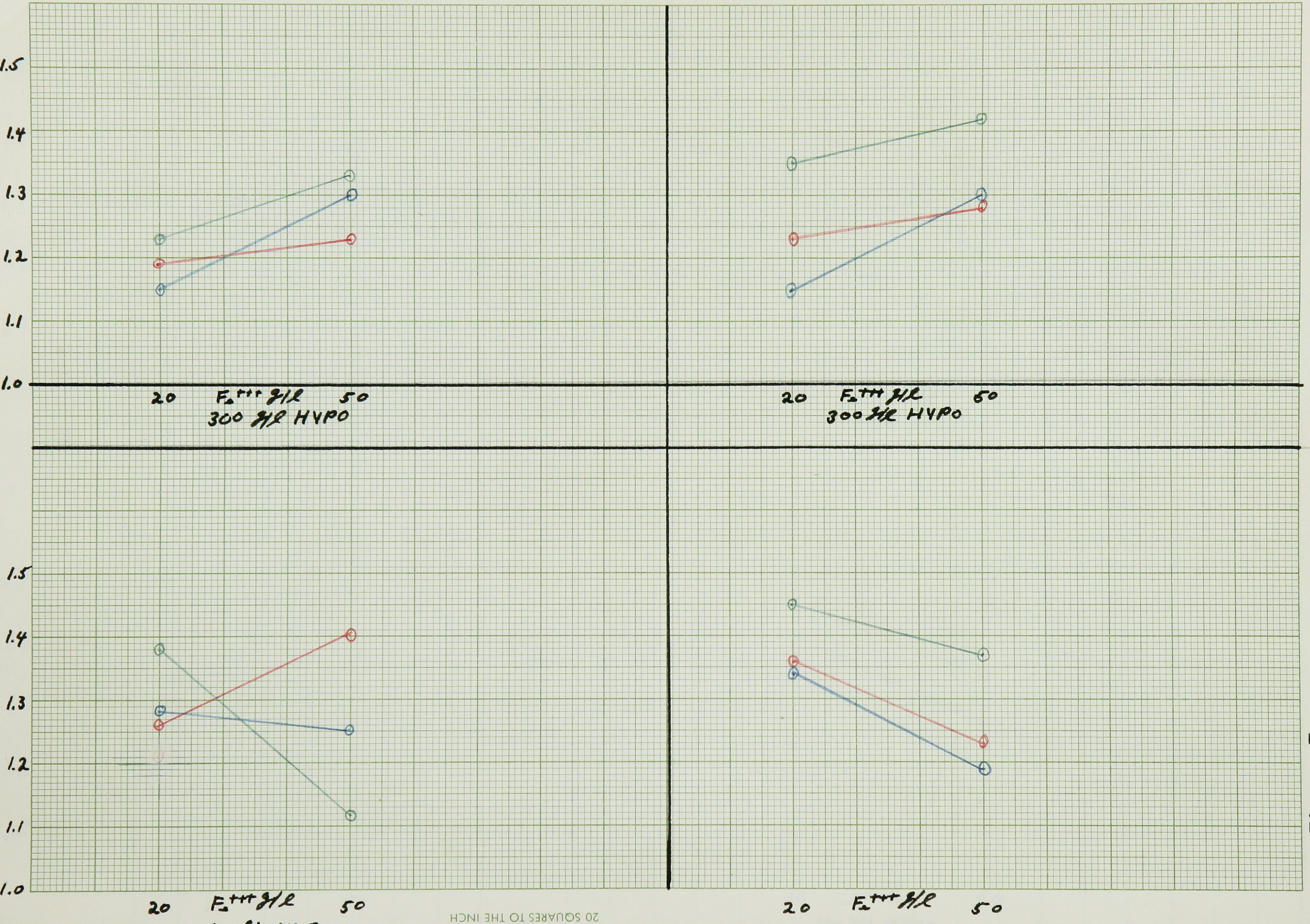


Figure 7

Figure 7

EFFECT OF BLEACH-FIX ON D. MAX

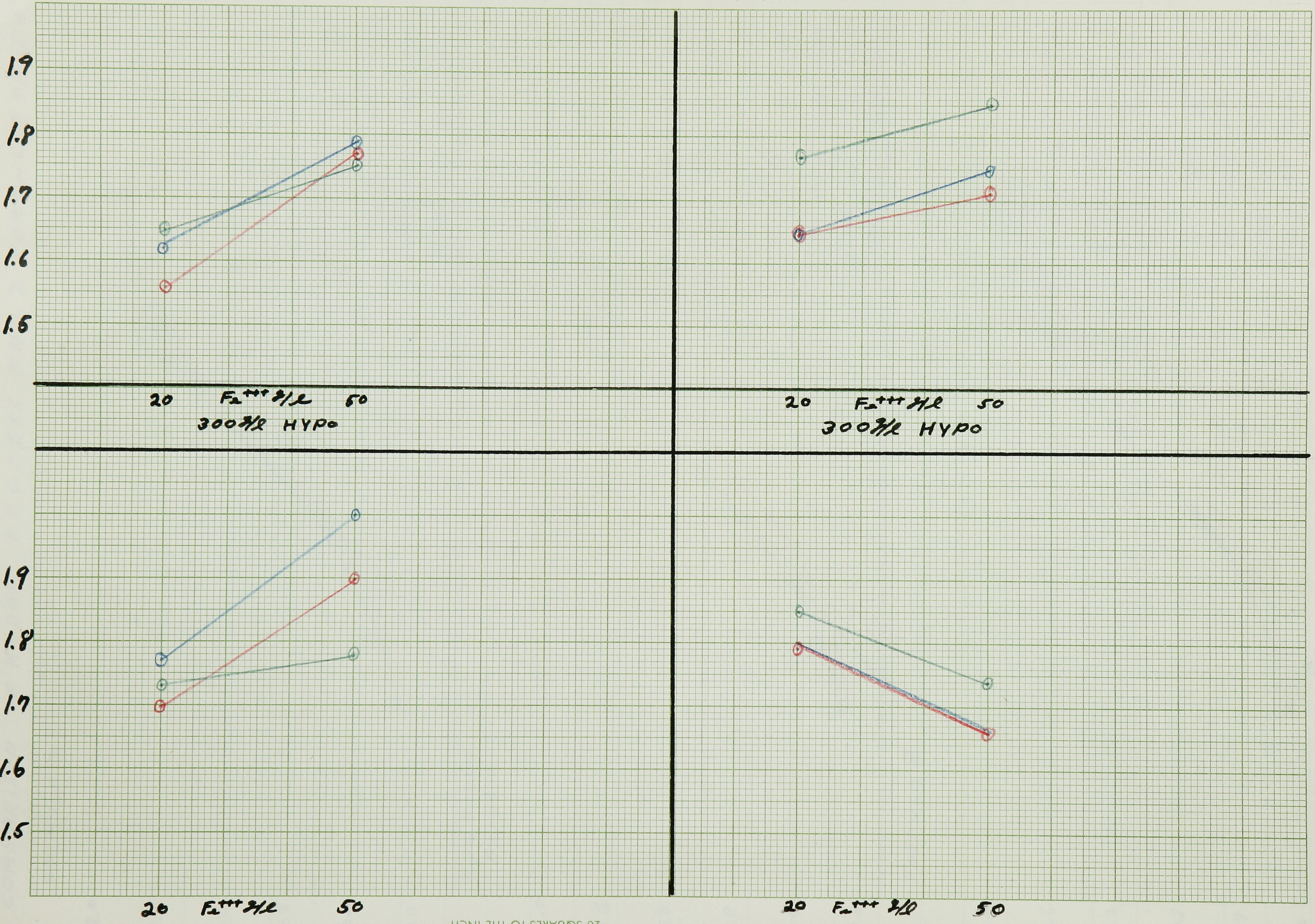
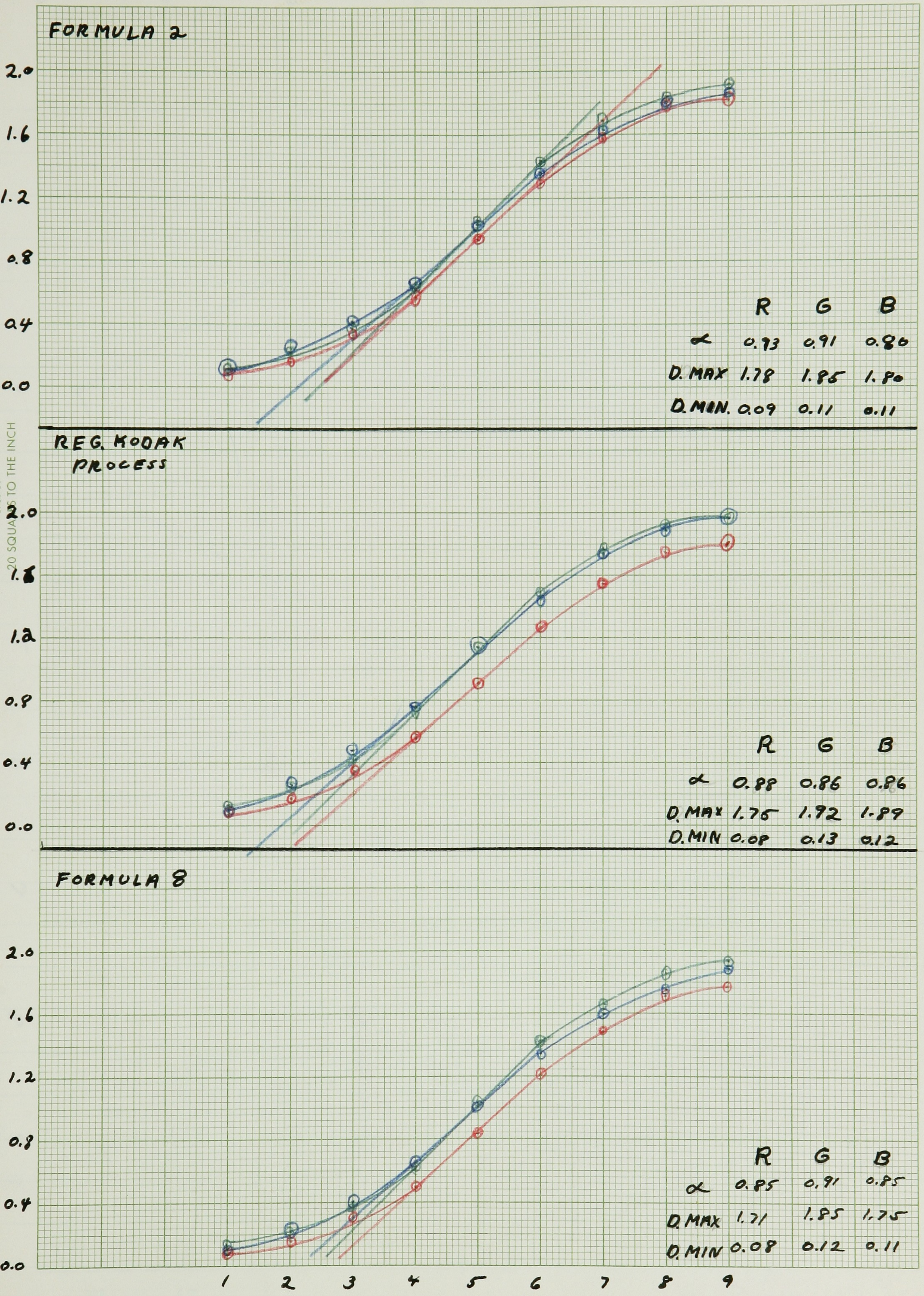


Figure 8

COMPARISON OF KODAK PROCESS AND 2 FORMULAS OF INV. #2



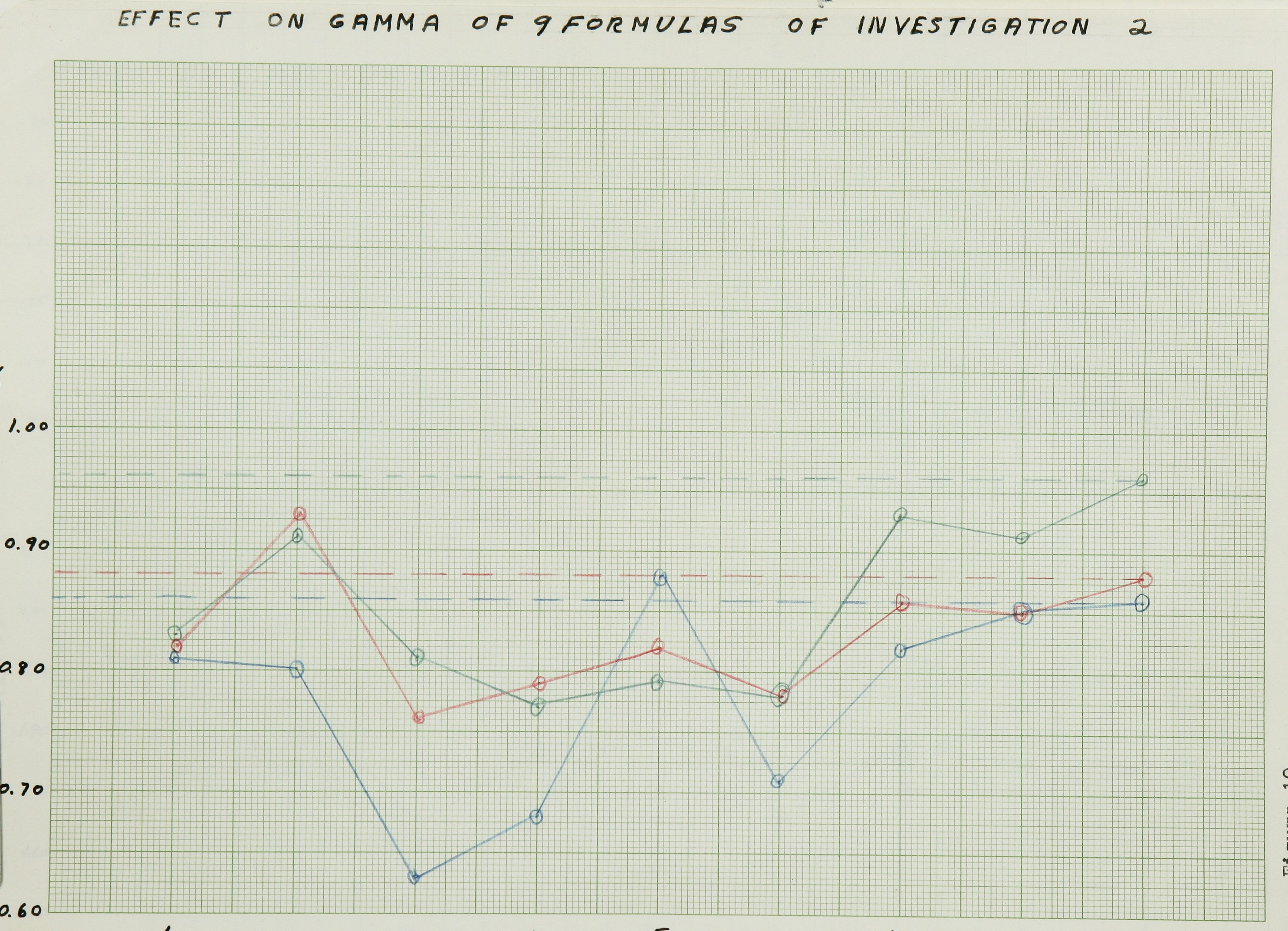

EFFECT ON GAMMA OF 9 FORMULAS OF INVESTIGATION 2
1.00
0.90
0.80
0.70
0.60

Figure 10

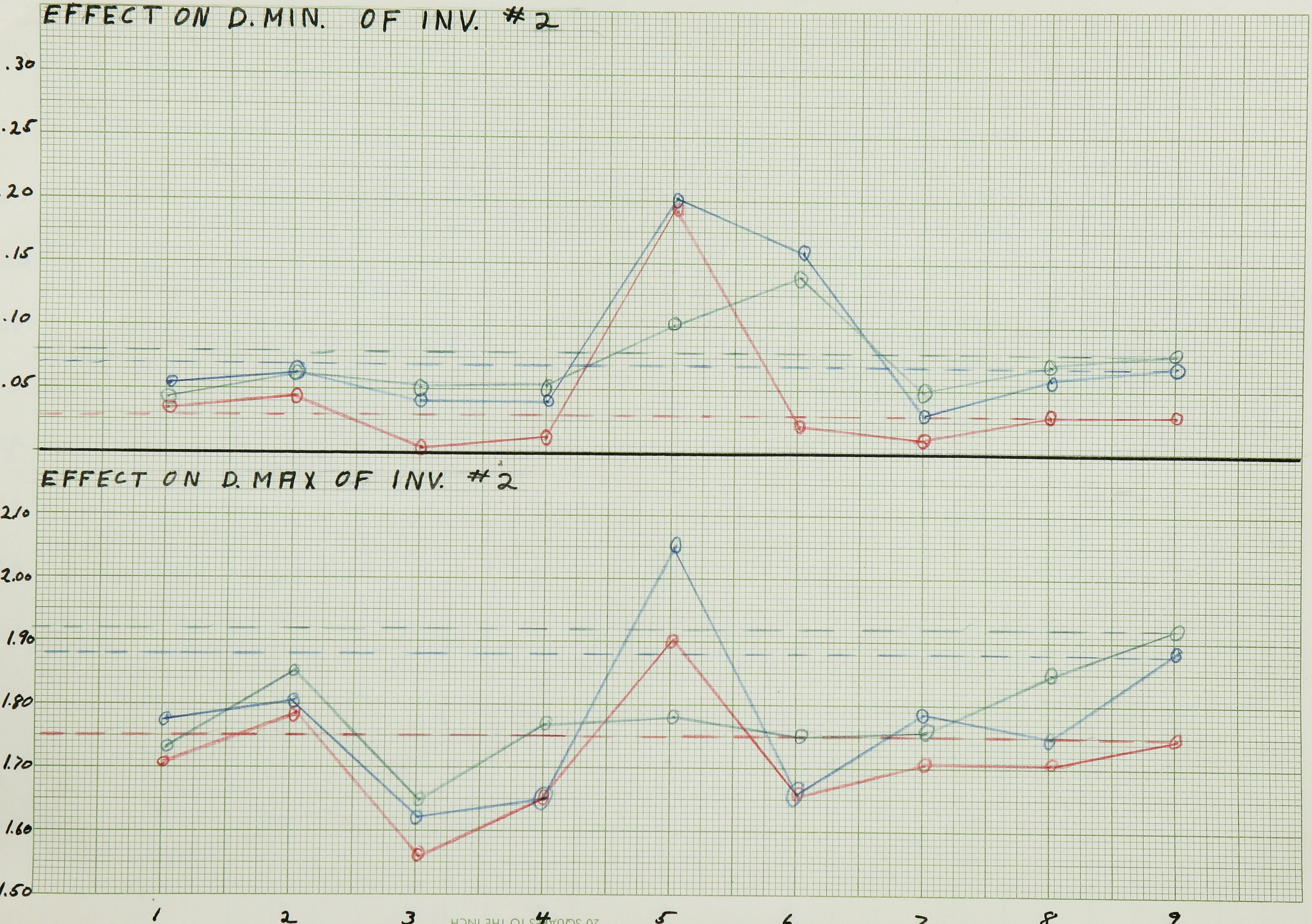

EFFECT ON D.MIN. OF INV. #2
.30
.25
.20
.15
.10
.05
EFFECT ON D.MAX OF INV. #2
2.10
2.00
1.90
1.80
1.70
1.60
1.50
1
2
3
4
5
6
7
8
9

Figure 11

EFFECT OF SO_3 ON BLEACH-FIX